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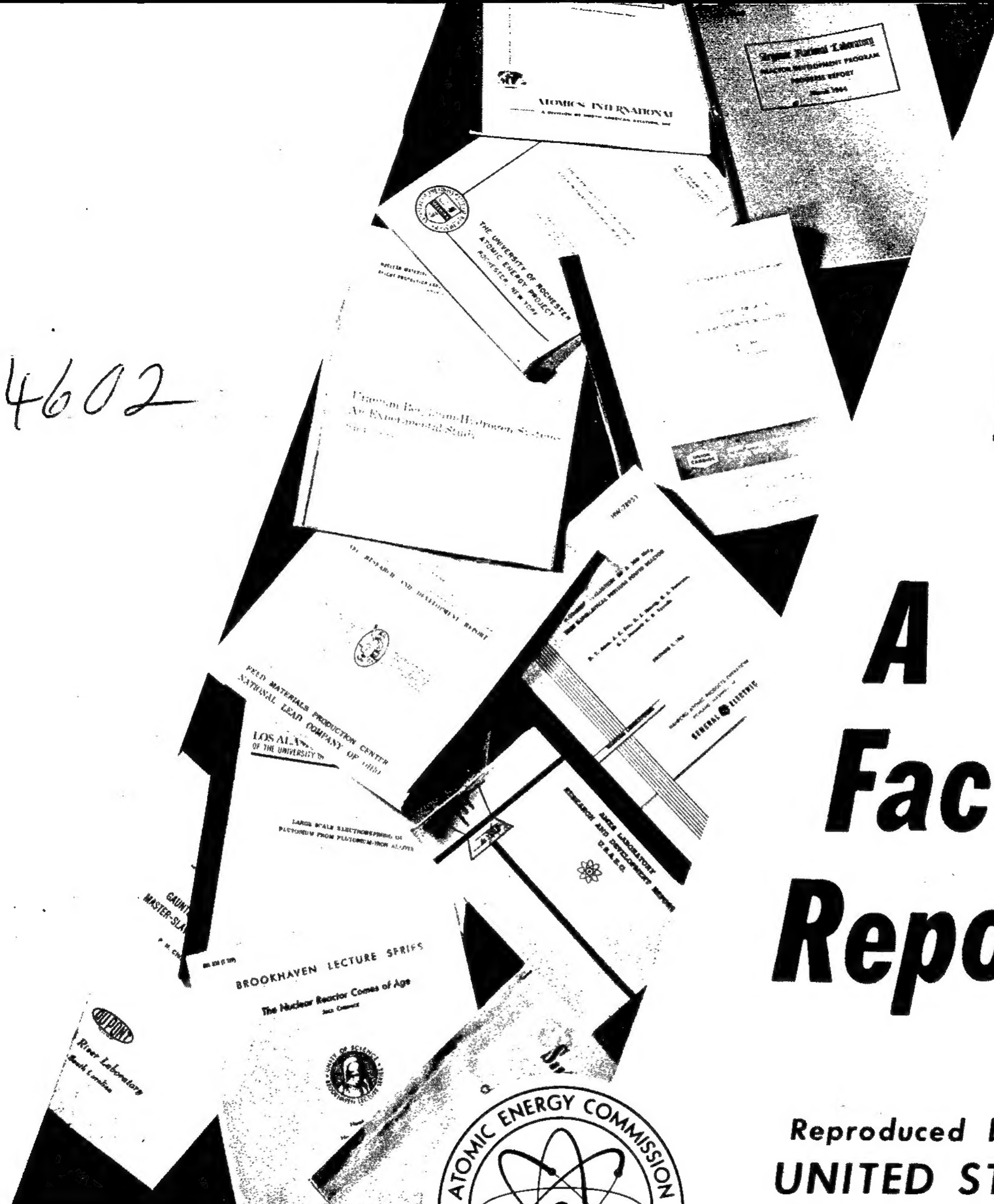

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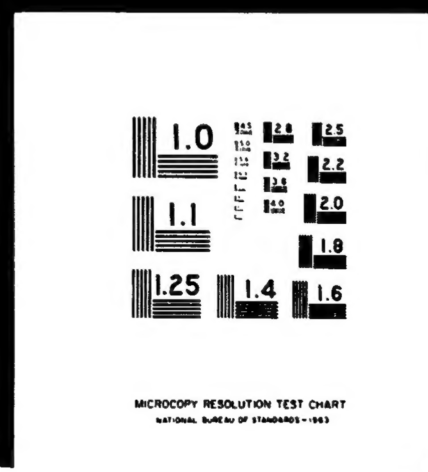

January 31, 1968

Final Report

INTERACTION OF LIQUID SODIUM WITH 304 STAINLESS STEEL

Prepared for:

FUELS AND MATERIALS BRANCH
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I INTRODUCTION

The effect of a liquid sodium environment on 304 stainless steel has important engineering significance because of the potential use of this liquid-metal solid-metal system in fast breeder reactors. It is well known that the metallurgical, mechanical, and chemical properties of most solid metals are influenced in varying degrees by intimate contact with a molten metal environment. The nature and degree of property deterioration are determined by a large number of variables such as: chemistry of the respective components, impurity levels, thermo-mechanical history and grain size of the solid metal, temperature, both external and internal (residual) stress levels, the nature and morphology of surface films, etc.

In recent years, considerable research effort has been expended in fundamental investigations of corrosion and embrittlement phenomena. In several cases, the nature and mechanism(s) of liquid metal interaction have been identified. This knowledge has permitted more effective use to be made of these solid-metal liquid-metal systems merely by instituting proper control of one or more of the metallurgical or environmental parameters.

The metallurgical behavior of certain steels in molten sodium environments is not presently understood. There is conflicting evidence on the liquid sodium penetration of grain boundaries in polycrystalline type 304 stainless steel.

The detection of grain boundary penetration is conventionally accomplished by metallographic analyses. The occurrence and extent of a second phase along existing grain boundaries is readily apparent.

When studying the extent of penetration of a metal with a low melting point (e.g., Na, Mp 97.8°C), results are questionable, since grain boundary penetration is accompanied by surface diffusion and grain-boundary "tunnel" diffusion, and the two processes cannot be easily distinguished. In addition, optical metallographic analysis lacks the resolution necessary to differentiate between conventional diffusion processes and mass transport by "wetting" along freshly severed grain boundaries.

Grain boundary penetration by a liquid metal in a thin metal foil is readily observable in the electron microscope.[1] Transmission electron microscopy allows the differentiation between the various bulk, grain boundary, grain-boundary "tunnel," and surface diffusion processes. It possesses the necessary resolution to detect very small cracks, and to identify possible mass transport by wetting. Electron diffraction analyses can also be performed in the electron microscope on the specimen area examined by transmission microscopy without disturbing the specimen. Thus, crystallographic orientations in a particular grain, the disorientation across a grain boundary, or the presence of another phase along grain boundaries can be determined and directly related to observations of grain boundary penetration.

Start

The advantages inherent in the electron microscopy method suggested its use in the present study. Three tasks were to be undertaken: In Task 1, relatively pure liquid sodium was to be brought into contact with a clean, ion-bombarded 304 SS surface and reacted with the steel at 1200°F for periods of time up to one week. The samples were then to be thinned, after exposure to the sodium to a thickness suitable for transmission electron microscopy. They were then to be examined in the electron microscope.

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[1] Goggin, W. R., and J. W. Moberly, "Direct Observations of the Liquid Metal Embrittlement of Aluminum by Gallium," Trans. ASM, 59, p 315 (June 1966).

In Task 2, thin foils of stainless steel were to be placed in contact with small amounts of sodium and introduced into the electron microscope. The sodium was to be melted with the electron beam and transmission microscopy techniques were to be used to observe any reaction that might occur. This method was used successfully in determining the influence of liquid gallium on the fracture behavior of aluminum.

The final task involved the examination of 304 SS foils after their exposure to sodium in a sodium loop at Argonne National Laboratories. These samples were to be supplied by SRI and, after exposure, were to be returned for electron microscopic examination at the Institute.

This report describes the progress we have made to date in completion of the above tasks. For reasons that will be explained in the report, some modification of the methods of carrying out the program were necessary. For example, prethinned foils were used in Task 1, rather than attempting to thin the foil after exposure. Also, in the *in situ* testing program, it was considered advantageous to evaporate a sodium film onto the foil within the microscope instead of melting a solid pellet of sodium with the electron beam.

In spite of the experimental difficulties associated with handling sodium under conditions of high temperature and purity, considerable progress was made in these tasks. Methods were developed for reliably thinning stainless steel foils, for exposing the foils to sodium in an inert atmosphere, for subsequent cleaning, and for final examination of the foils in the electron microscope. At the time of writing this report, the most promising results have come from studies of the type described in Task 1. Definite evidence of attack and grain boundary corrosion has been obtained and electron microscopy studies reveal new features of sodium attack that are worthy of further study.

II EXPERIMENTAL PROCEDURE

A. Materials

The 304 stainless steel used for specimens in this investigation was annealed 0.010 in. sheet stock purchased from Ducommon Metals and Supply Co. All specimens were cut from one sheet.

Reactor grade sodium metal used in these studies was obtained from the MSA Research Corporation, Evans City, Pennsylvania. It was supplied in glass ampoules, each containing 1 or 5 g of the metal. Table I shows the results of an emission spectrographic analysis of a sample of sodium typical of that in the ampoules. While every effort was made to maintain this standard of purity in our experimental work, it must be noted that changes in impurity levels of some elements (notably, oxygen) could have occurred.

Table I

TYPICAL IMPURITY LEVEL OF VARIOUS ELEMENTS IN REACTOR GRADE SODIUM

Element	ppm	Element	ppm	Element	ppm
Fe	3	Cr	1	Sr	1
B	5	Si	15	Ba	3
Co	5	Ti	5	Ca	5
Mn	1	Ni	1	Li	1
Al	2	Mo	5	Na	
Mg	1	V	1	K	40
Sn	5	Be	1	Rb	10
Cu	2	Ag	1	Cs	
Pb	5	Zr	10	O_2	10
Y	5	Bi	5	C	22

B. Sample Preparation and Microscopy

The microscope used was a Hitachi Model HU-11 with a type HH-2 hot stage. This microscope has a resolution of 5 Å, a magnification range of 400X to 100,000X, and selected area diffraction and specimen tilting capabilities. The hot stage has a range from room temperature to 1000°C.

Foils were made from 1 x 2 inch blanks cut from 0.010 inch annealed 304 SS stock. These blanks were thinned by the window method using Stoner-Mudge S-1275-801 vinyl maskant.

The electropolishing solution was 60% phosphoric acid - 40% sulfuric acid, operated at 65°C ± 15°C. The bath was made up in 200 ml portions as required. Each portion was sufficient to thin four specimens.

As each hole in the specimen appeared, due to nonuniform electropolishing, more maskant was added. This reduced the size of the window while maintaining a rectangular area. Periodically, the accumulation of maskant was stripped and the specimen was remasked. Ten to twelve cuts were required to obtain a foil. During the last three cuts the sample was masked completely on one side and polished on the other. After the final cut, the maskant was peeled off and the specimen was stored in ethanol. An "as-polished" sample was removed from each foil at this time by cutting with a scalpel blade against a Lucite block under ethanol. Depending upon the amount of supporting metal desired, the foil was removed from the sample either by this cutting method or with scissors.

The prepared foils were mounted between 75 mesh copper grids.

C. Method of Exposure

1. Static Exposure Testing

Most exposure tests of thinned stainless steel foils to sodium at about 1200°F were carried out in a small furnace operating within a conventional vacuum system. The vacuum system was equipped with diffusion and mechanical pumps, vacuum gauges, various rotational and translational seals, thermocouple feed-throughs, a high voltage feed-through, and a port for the admittance of high purity argon gas. The system is shown in Fig. 1.

The furnace that held the sodium was constructed from 304 stainless steel (Fig. 2). The close-fitting cover to the furnace, also

FIG. 1 VACUUM CHAMBER FOR STATIC EXPOSURE TESTING

FIG. 2 STAINLESS STEEL FURNACE FOR STATIC EXPOSURE TESTING

made of 304 stainless steel, could be removed and replaced by means of manipulators in the vacuum system. To minimize heat losses, a series of heat shields were placed around the furnace. Since the only materials in contact in the furnace were stainless steel and sodium, contamination by material transfer between dissimilar materials was eliminated.

In order to remove oxide surface films and other contaminants from the foil surface, the vacuum system included a high voltage electrode which permitted ion-bombardment cleaning. High purity argon gas was used for this purpose. This step was used in the preparation of the foil to improve wetting of the stainless steel surface with the sodium. Experiments showed, however, that this procedure was unnecessary, since complete wetting was easily achieved without ion-bombardment cleaning, and furthermore, the ion-bombardment process actually damaged the edges of the foil by causing local heating.

SS

Start In a typical experiment, a thinned stainless steel foil was placed in the vacuum chamber evacuated to 10^{-5} torr. The furnace was degassed by heating to red heat, and the vacuum chamber was backfilled with high purity argon gas to a pressure of about 700 mm. The sodium ampoule was broken in the chamber; the sodium was heated to the molten state by radiation from the furnace. The liquid sodium was then poured into the furnace to completely cover the foil. The lid of the furnace was then replaced and the liquid was sodium brought to operating temperature (1200°F). Foils were exposed to liquid sodium for various periods of time, up to about 110 hours, with this procedure. The furnace was allowed to cool at the completion of the experiment, and the foil was removed for cleaning.

The procedure for removing the sodium from the foil surface made use of a Soxhlet extractor (Fig. 3). With this technique the sodium-covered foil is placed on a shelf in the middle section of the apparatus, where it was washed with solvent (alcohol, water/alcohol, or water and isopropanol) which returns from the condensor placed above the extractor. When the solvent level in the extractor and in the side arm reach a certain level, the solvent from the extractor returns to the flask at

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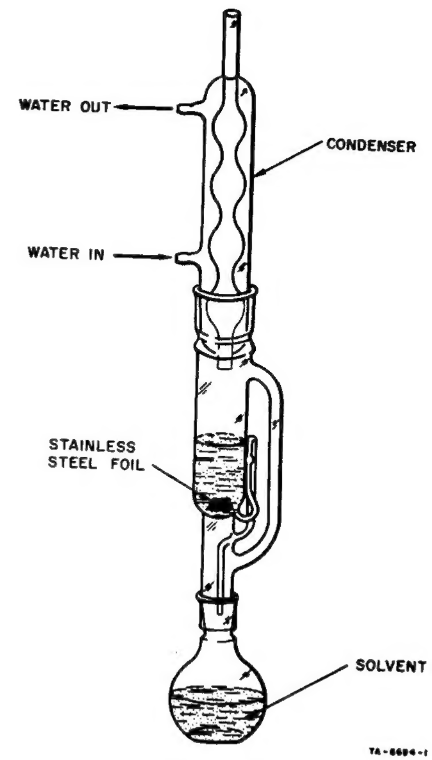

FIG. 3 SOXHLET EXTRACTOR

the bottom of the apparatus and the process repeats itself. The advantage of this apparatus is that the foil is only exposed to pure solvent, and reprecipitation of impurities from the solvent bath is practically eliminated. Optical examination of the foil cleaned in the above manner indicated a perfectly clean surface.

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Two other methods of exposing the foils were examined but neither was as satisfactory as the above technique. The first involed the use of a furnace with a double gasket. The intention was, first, to effect a temporary vacuum-tight seal between the two halves of the furnace by a conventional O-ring and then, later, to apply pressure on an inner stainless steel gasket and obtain a permanent seal when the temperature was raised to 1200°F. Accordingly, the furnace was filled with sodium in the vacuum bell jar, and the two parts of the furnace were brought together and sealed. The furnace was then brought out of the vacuum bell jar and sufficient pressure was applied to obtain a seal on the inner stainless steel gasket. It was realized, of course, that at high temperatures the outer O-ring gasket would decompose; however, if the stainless steel gasket held, then no contamination of the contents of the furnace would result. All attempts to use this procedure were unsuccessful. Usually, the cause of the failure was an inadequate seal on the stainless steel gasket which allowed carbonaceous products to enter the furnace and contaminate the sodium.

Another procedure involved sealing up several grams of sodium in a stainless steel tube (5/8 inch diameter) which was closed at one end; the other end could be closed through a flange and gasket arrangement. Again, the sodium was loaded into the tube in the vacuum bell jar. The tube was then removed from the vacuum system and crimped closed near the flange. The flange part of the apparatus was then cut off and the tube welded. The tube and its stainless steel foil and sodium contents was then heated in a furnace to 1200°F. Because of limited time, this procedure was not used extensively.

2. In Situ Testing

The initial effort was to place a small chip of sodium on a stainless steel foil mounted in one of the electron microscope specimen holders. This operation was performed under an optical microscope in an argon filled glove box with metallic sodium getters. The specimen

holder, in the form of a short cylinder, was such that both sides of the foil could be covered with sodium-dried benzene. By this means the sample was transferred to the microscope sample chamber. The benzene was pumped off during the evacuation of the microscope. The transfer required only a 30-second exposure to laboratory atmosphere.

One difficulty encountered in this method was to obtain just the right size sodium chip. This problem and the problem of oxidation led to the attempt to vapor deposit sodium directly onto the foil in the microscope.

Vapor deposition of sodium on the foil required the construction of a sodium evaporator to replace the microscope's specimen chamber window. This permitted sodium to be vaporized directly onto the foil in the microscope, thereby offering several advantages: the sodium on the foil is freshly distilled with no contact with air, and the sodium film is uniform in thickness and is controllable to within 100 Å.

The design of the evaporator is such that there is no sodium contamination of the microscope and the foil can be viewed immediately after evaporation, i.e., within a few seconds. Unfortunately, even with a residual gas pressure within the microscope of 2×10^{-5} torr, oxidation of the evaporated sodium film does occur on exposure. These experimental difficulties did not allow satisfactory results to be obtained.

Based on previous SRI experience in passivating alkali metal and alkaline earth thin films, it may be possible to overlay the sodium with a non-reactive film to permit long term in situ measurements with low contamination.

3. Exposure to a Sodium Loop

In order to examine the attack of sodium on stainless steel foils under dynamic conditions, arrangements were made to expose several thinned foils to sodium loop at Argonne National Laboratory. We were helped in this task by the capable assistance of Dr. F. A. Smith of Argonne.

Initially, three foils prepared according to the method described in Section II, B were sent to Argonne so that they could determine the mechanical adequacy of their foil holder. Later, twelve additional foils were sent to Argonne. These twelve foils fell into three categories according to the way in which the final cleaning operation was accomplished.

1. Foils numbered 1 through 4 were washed after thinning in distilled water, then in pure alcohol, and were dried.

2. Foils numbered 5 through 8 were washed after thinning in alcohol and were dried.

3. Foils numbered 9 through 12, after treatment according to (1) above, were ion-bombarded for 3 minutes.

The foils were shipped to and from Argonne in argon-filled polyethylene bags to minimize surface oxidation of the stainless steel. To date, only one foil has been returned to SRI for electron microscopic examination. The following information on the method of exposure of the foils, and its subsequent cleaning and shipping was kindly supplied in a letter to us from Dr. Smith.

a. Sodium Exposure Apparatus. Figure 4 shows the unassembled parts of a holder for the thinned foil.

The center heavy picture frame is sized for the O.D. dimensions of the foil, including heavy edges. Stainless steel fine wire mesh-woven screen is lightly fitted to hold the foil assembly "snug" in the center frame. This is accomplished by bolting the "right hand" and "left hand" frames to the center, or foil-holding frame.

b. Technique of Sodium Exposure. The principal purpose of our initial test was to determine that the foil would remain intact during sodium exposure. We were not concerned with sodium quality or other factors relating to keeping an inert atmosphere over the sodium exposed sample. With this in mind, a small available static tank, about 10 inches high by 8 inches I.D., was used for sodium exposure.

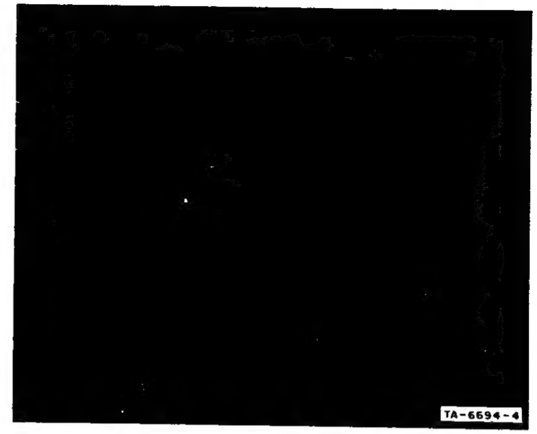

FIG. 4 SPECIMEN HOLDER FOR SODIUM LOOP EXPOSURE

The tank originally had a 1/8-inch pipe-size drain line with a bellow-sealed needle valve connected to a heated sodium dump tank. Since there was no provision for an inert gas glove box for specimen handling directly mounted to the specimen exposure tank, the following steps were taken:

(a) The sample was unbagged in air and installed in the sample holder.

(b) A stainless steel wire was fastened to two of the bolts of the assembled specimen holder and suspended from a top-bolted and gasketed flange of the exposure tank.

(c) Sodium exposure was from Oct. 31, 1967 to Nov. 7, 1967 at 1200°F.

(d) Sodium was cooled to 600°F for dumping. Part of the sodium drained before the small needle valve plugged. We believe the foil and holder were still submerged at this time. The sodium in the specimen exposure tank was frozen with argon blanket gas at $\sim$ 2 psi. The 1/8-inch pipe drain line was replaced with a 1-inch drain line and a 1-inch gate valve. The system was reheated to 1200°F and drained.

(e) The foil and holder were removed, in air, and the foil holder was immediately placed in butyl alcohol. According to observation of H_2 generation, it took about five hours for all available sodium to react.

(f) The sample holder was disassembled in air and placed in a small portable argon-purged dry box.

(g) The sample was bagged inside an argon-purged dry box. At this step in bagging, the center thin section became detached from its own heavier picture frame. Packing and shipment concluded this test.

The following conclusions and recommendations were also communicated to us by Dr. Smith:

1. The foil holder is adequate for support of thin foils in sodium, but the sample removal sequence needs improving.
2. Steps have been taken to include a small portable dry box directly on top of the sodium exposure vessel.
3. All handling operations of the foil from step (a), unbagging, to step (g), rebagging for shipment, can be conducted without an air atmosphere contacting the sample.
4. In addition, a sodium system filling technique has been developed to use diffusion cold-trapping to permit sodium filling of the test or specimen exposure vessel with sodium cold-trapped at 220°F. The 220°F diffusion cold-trapped sodium is admitted directly to the vessel at 550°F.

c. Present Status of the Sodium Loop Work. The dry box is complete and assembled to the sample test vessel. The sodium has been diffusion cold-trapped and the test vessel is filled with sodium.

The remaining two "experimental" foils were to be exposed to the new test system. One of these foils was to be returned to SRI for analysis; the other foil would be retained for analysis by ANL.

The remaining twelve foils were to be exposed as follows:

(a) Six foils in D-308 hot loop (circulation).

(b) Six foils in modified (static) system described above.

To date, only the first exposed foil has been returned to SRI. However, this foil was severely oxidized in shipment, so further studies were not possible.

III RESULTS AND DISCUSSION

This investigation has shown that an electron microscopic study of the corrosion behavior of thinned stainless steel foils by sodium has many advantages over previous methods involving the use of bulk stainless steel samples. Thus, several phenomena such as grain boundary corrosion, precipitation reactions, and solution behavior of the stainless steel foil have been examined in a way which is not possible with other techniques. While direct evidence of attack by the liquid sodium has been observed, additional studies will be necessary to fully determine the compatibility of 304 stainless steel with liquid sodium at 1200°F with this new technique.

Electron micrographs of annealed 304 stainless steel foils, as electropolished, are shown in Figs. 5-7. The grains are generally equiaxed and the grain boundaries are well defined. The dislocation density in the foils is low, but numerous annealing twins are observed. The edges of the foils are very smooth after electropolishing (Fig. 6). These micrographs are typical of the 304 stainless steel foils used in all tasks of the experimental investigation.

The static exposure (Task I) of 304 stainless steel in liquid sodium operating in the vacuum system was highly successful in revealing several phenomena. Initially, an ion-bombardment step was used to fully clean the surface of the metal to insure wetting by the liquid sodium. Unfortunately, during the ion bombardment treatment the temperature of the foil increased substantially, causing the metal to recrystallize in a very fine grain structure as seen in Fig. 8. At times the foils failed to recrystallize during ion-bombardment but recrystallized after heat treatments at 1200°F. Recrystallization of ion-bombarded foils was also induced by exposure to liquid sodium. In either case the resulting structure was too fine for subsequent observation of grain boundary attack by the liquid sodium. Consequently, the ion bombardment treatment was discontinued as a surface

FIG. 5 TRANSMISSION ELECTRON MICROGRAPH OF 304 STAINLESS STELL AFTER ELECTROPOLISHING

FIG. 6 TRANSMISSION ELECTRON MICROGRAPH OF 304 STAINLESS STEEL AFTER ELECTROPOLISHING. Micrograph shows pinhole (A) in grain boundary due to selected chemical attack. Fringes (B) are thickness contours.

FIG. 7 TRANSMISSION ELECTRON MICROGRAPH OF 304 STAINLESS STEEL FOIL AFTER ELECTROPOLISHING. Micrograph shows a single grain boundary and smooth foil edge.

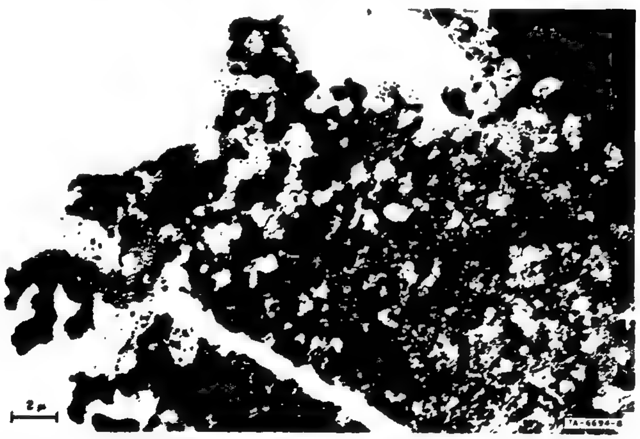

FIG. 8 TRANSMISSION ELECTRON MICROGRAPH OF 304 STAINLESS STEEL FOIL, AFTER ION BOMBARDMENT. The micrograph shows very fine grain structure which resulted from recrystallization due to excessive heating during ion bombardment treatment. Damage to the edge of the foil also occurred during this process.

cleaning procedure. This proved to be no hindrance to the experimental program, since with the method used it was found that the electropolished stainless steel foils were always wetted by the liquid sodium at temperatures above 700°F.

A satisfactory method of removing sodium from the exposed stainless steel surface was also demonstrated in our studies. For example, an electropolished stainless steel specimen that had been immersed in a sodium bath at 700°F for 10 minutes was cleaned of all traces of any surface deposit by the Soxhlet extraction procedure described earlier. (The temperature of 700°F was determined to be the lowest temperature at which it was certain that complete wetting of the foil surface by the sodium was achieved). Fig. 9 is an example of such a foil. No residue is seen on the surface or at the grain boundaries. In fact, the foil appears as clean, if not cleaner, than a freshly electropolished foil. In light of subsequent observations, the efficiency of the cleaning technique to remove all sodium (or sodium oxide) from the foil surface was very important.

304 stainless steel foils that were exposed to static liquid sodium at 1200°F for times of three to eleven hours were examined in the electron microscope. Several reactions between the stainless steel and the liquid sodium were observed. These include:

1. Grain boundary attack
2. General attack at foil edges
3. Formation of precipitates on the foil surface and at grain boundaries

Control specimens which were stored in ethanol, handled and given the same thermal treatment (1200°F), but without exposure to sodium showed no such effects.

The appearance of a foil after exposure to the liquid sodium at 1200°F for eleven hours is seen in Fig. 10. The precipitate, which is

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FIG. 9 TRANSMISSION ELECTRON MICROGRAPH OF 304 STAINLESS STEEL AFTER EXPOSURE TO LIQUID SODIUM AT 700°F. The micrograph reveals a thoroughly clean foil having no residual sodium. The curved black lines are extinction contours due to the bending of the foil.

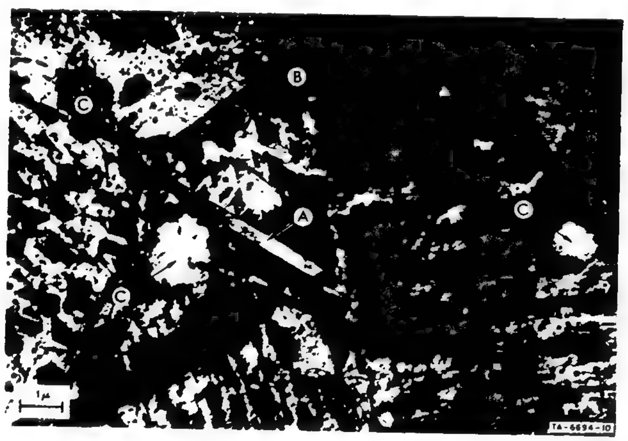

FIG. 10 TRANSMISSION ELECTRON MICROGRAPH OF 304 STAINLESS STEEL FOIL, AFTER THREE HOURS EXPOSURE TO LIQUID SODIUM AT 1200°F. Micrograph shows a geometrical surface precipitate over nearly all grains, but not on twin (A). Grain boundary attack has occurred along boundary (B). Enlargement of a pinhole in the foil has occurred at (C).

deposited on almost all the grains, appears dark because it is thick enough to absorb all the electrons that otherwise would pass through the foil. The deposit always has a geometrical shape, which varies from grain to grain, often a grain is heavily deposited, but a twinned section of the same grain is relatively free of deposit. So far it has not been possible to identify this deposit by transmission electron diffraction. In view of the fact that stainless steel foils can be cleaned so successfully after exposure to liquid sodium at and below 700°F, it is felt that this precipitate is neither sodium nor sodium oxide. One grain boundary shown in Fig. 10 has been attacked by the liquid sodium. Rather large holes with very ragged edges can also be seen in this micrograph. These holes may well have been small pinholes in the electropolished foil (Fig. 6) that have been enlarged by attack of the liquid sodium metal. The grain boundary attack can be more clearly seen in Fig. 11, which is a higher magnification micrograph of the same area of the foil. Only a few of the grain boundaries were attacked, but no detailed orientation studies were made to determine which boundaries were involved. Figs. 12 and 13 reveal grain boundaries that have been severely attacked, leaving the edges with the characteristic ragged effect. This etching behavior is always observed at the edges of the foil: thus, a very smooth edge (Fig. 7) becomes ragged and irregular after exposure to liquid sodium at 1200°F (Figs. 14 and 15).

5 5

The extent to which grain boundary attack occurs is not fully understood. It is also not clear whether significantly more attack occurs with longer exposure times than with shorter exposure times. In all foils examined, some of the boundaries are totally destroyed and holes extend through the thickness of the foil. Without doubt, much longer exposures (several days) would cause more severe attack. Prolonged exposures have not been possible with the present experimental system because of excessive evaporation of the sodium.

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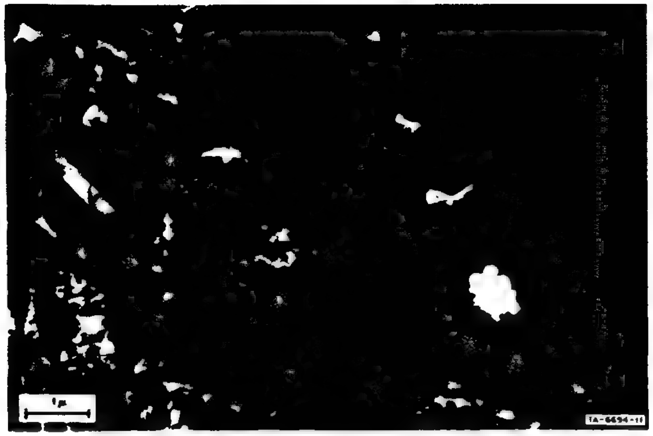

FIG. 11 TRANSMISSION ELECTRON MICROGRAPH OF 304 STAINLESS STEEL FOIL AFTER THREE HOURS EXPOSURE TO LIQUID SODIUM AT 1200°F. This higher manification micrograph of the area shown in Fig. 10 shows the grain boundary attack more clearly.

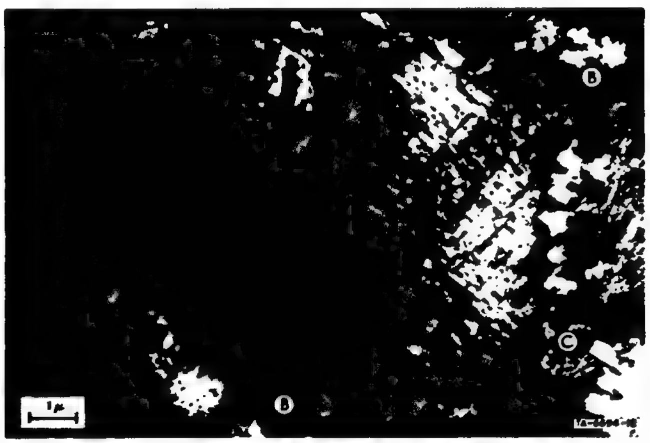

FIG. 12 TRANSMISSION ELECTRON MICROGRAPH OF 304 STAINLESS STEEL FOIL AFTER THREE HOURS EXPOSURE TO LIQUID SODIUM AT 1200°F. Micrograph reveals severe grain boundary attack along several boundaries (B) and etching of hole (C).

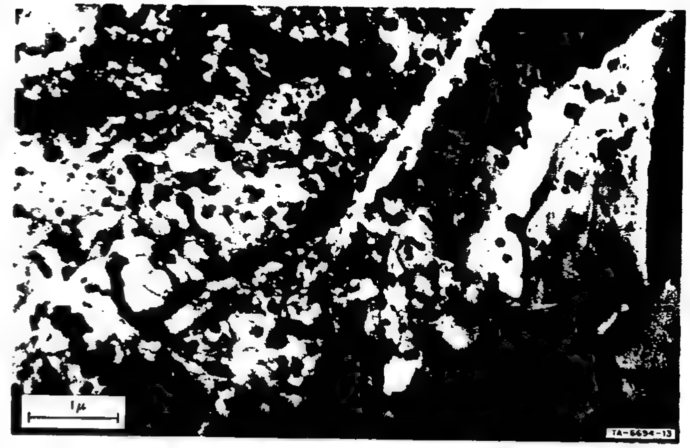

FIG. 13 TRANSMISSION ELECTRON MICROGRAPH OF 304 STAINLESS STEEL FOIL AFTER ELEVEN HOURS EXPOSURE TO LIQUID SODIUM AT 1200°F. Structure shows a severely attacked foil.

FIG. 14 TRANSMISSION ELECTRON MICROGRAPH OF 304 STAINLESS STEEL FOIL AFTER FIFTEEN HOURS EXPOSURE TO LIQUID SODIUM AT 950°F. Micrograph shows holes etched in surface by liquid sodium. The very ragged edge of the foil has also been severely attacked.

FIG. 15 TRANSMISSION ELECTRON MICROGRAPH OF 304 STAINLESS STEEL FOIL AFTER SIX HOURS EXPOSURE TO LIQUID SODIUM AT 1200°F. Micrograph shows attacked foil edge as well as surface and grain boundary deposit.

The nature of the residual surface precipitate can vary greatly from one experiment to the next. This is clearly seen by contrasting the structures in Figs. 15 and 10. In Fig. 16, most grains are relatively free of this deposit, only a few grains having a surface precipitate. This figure illustrates the dependence of the precipitate upon the orientation of the stainless steel grain. A section of a given foil is free of precipitate but a twinned section of the same grain is heavily deposited. Another striking observation in this micrograph is the preferential deposit of the precipitate along grain boundaries. A higher magnification micrograph of the same foil, Fig. 17, clearly illustrates this. At times, the precipitate appears to be deposited totally within the grain boundary. This is shown in Fig. 18, which also reveals that the twin boundaries remain clean. This lack of deposit in or at twin boundaries is always observed.

FIG. 16 TRANSMISSION ELECTRON MICROGRAPH OF 304 STAINLESS STEEL FOIL AFTER ELEVEN HOURS EXPOSURE TO LIQUID SODIUM AT 1200°F. A preferential deposit along grain boundaries is evident throughout. Sections of some grains have fairly heavy surface deposits (A), whereas twinned sections of the same grains are relatively clean (A').

FIG. 17 TRANSMISSION ELECTRON MICROGRAPH OF 304 STAINLESS STEEL FOIL AFTER ELEVEN HOURS EXPOSURE TO LIQUID SODIUM AT 1200°F. Micrograph clearly shows geometrical grain boundary precipitate.

FIG. 18 TRANSMISSION ELECTRON MICROGRAPH OF 304 STAINLESS STEEL FOIL AFTER ELEVEN HOURS EXPOSURE TO LIQUID SODIUM AT 1200°F.
Structure shows selective gain boundary precipitate. Note that the twin boundaries are free of deposit.

Fig. 19 shows a region of an exposed foil that is relatively free of both surface and grain boundary deposit, compared with the structure in Fig. 20. Foils such as that in Fig. 19 have, after initial cleaning and examination, received a second and more vigorous cleaning without reducing the amount of deposit observed. Variations in surface deposits therefore are not solely attributable to the efficiency of the cleaning technique.

Considering the differences in the appearance of the deposits, it appears that more than one precipitate may be involved. Although attempts were made to keep the exposure experiments identical, except for time, it may be that the purity of sodium varied. If this occurred, it is not unlikely that the extent of reaction between the liquid sodium and the 304 stainless steel also varied.

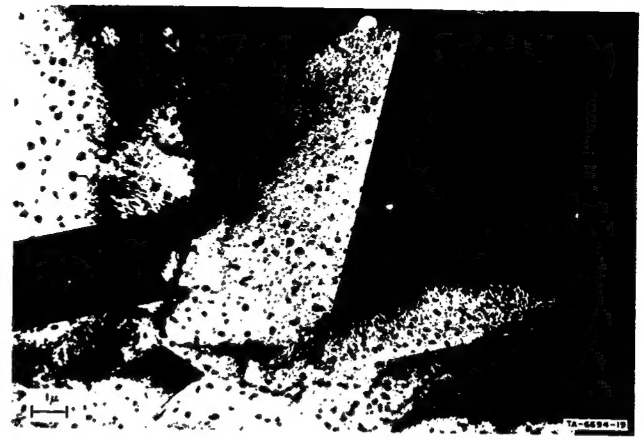

FIG. 19 TRANSMISSION ELECTRON MICROGRAPH OF 304 STAINLESS STEEL FOIL AFTER FIFTEEN HOURS EXPOSURE TO LIQUID SODIUM AT 950°F.
Surfaces and grain boundaries are relatively free of deposit.

FIG. 20 TRANSMISSION ELECTRON MICROGRAPH OF 304 STAINLESS STEEL FOIL AFTER SIX HOURS EXPOSURE TO LIQUID SODIUM AT 1200°F.
Heavy deposits occur on surface and at grain boundaries.

The precipitates observed in our work may well be identical with the lamellar phases described by Ratz and Brickner[2] in their work on the effect of liquid sodium on welded 304 stainless steel pipe. Although these lamellar surface precipitates were not fully identified, X-ray analysis suggested that they could be $Cr_{23}C_6$, Cr_3C_2, Cr_2N, or some combination of all three compounds. It is not known when the precipitates formed. They may be reaction products formed during high temperature exposure, or they could have precipitated when the system was cooled from 1200°F. This could be due to the decreased solubility of the various elements in the liquid sodium at lower temperature.

What effect these surface precipitates have on grain boundary attack at 1200°F has yet to be determined. It is known, however, that 304 stainless steel structural elements do show increased grain boundary attack if they are re-exposed to liquid sodium for a second time. The cause of this increase in grain boundary attack is not clear. It has been suggested that the problem arises from incomplete cleaning of sodium from the stainless steel surface after removal from the sodium environment. It is believed that the residual sodium film becomes oxidized and that this contaminates the liquid sodium when the stainless steel element is returned to the liquid metal system. However, it may be that the increased susceptibility to grain boundary attack is a consequence of other precipitates on the stainless steel surface. If this is the case, regardless of the care taken in the sodium cleaning step, accelerated attack of the stainless steel by liquid sodium would still occur upon subsequent exposure.

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[2] Ratz, G. A., and K. G. Brickner, "Effect of Liquid Sodium on Welded AISI Type 304 Stainless Steel Pipe," to be published in Nuclear Applications.

IV CONCLUSIONS

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The experimental technique of transmission electron microscopy in stainless steel foils after exposure to liquid sodium at 1200°F has been successful in revealing several liquid-sodium, stainless-steel reactions. This technique allows the observation of reactions that were undetectable by optical metallography. In particular it has been observed that:

1. After exposure of the foils at 1200°F, severe grain boundary attack occurs.

2. Surface precipitates, thought not to be sodium or sodium oxide, are observed on the foils.

3. The precipitates, which may consist of one or more compounds, are also formed along and within the grain boundaries and have a dependence on orientation of the 304 stainless steel grains.

4. Electron diffraction studies have not as yet identified the composition of these precipitates.

5. Finally, transmission electron microscopy is an excellent technique for fully evaluating any cleaning procedure for metal foils after liquid sodium exposure.

end

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